

AN EVALUATION OF SELECTED BLEACHING TREATMENTS
SUITABLE FOR HISTORIC WHITE COTTONS

by

ZOE KATHERINE ANNIS

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Approved by:

Barbara M. Reagan
Major Professor

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INTRODUCTION

The discoloration of undyed, historic cotton textiles is attributed to a variety of factors such as body oils, perspiration, dirt, atmospheric contaminants, and aging. Depending on the physical and chemical condition of the fibers, the appearance and whiteness of cotton textiles may be substantially improved by wet cleaning and bleaching treatments. Literature pertaining to bleaching methods applicable for cleaning and restoring the whiteness of historic textiles and the damaging effects of such treatments is limited; thus, a study concerned with the effects of bleaching methods on historic cotton is significant. The purpose of this study was to evaluate selected bleaching treatments on naturally yellowed, undyed cottons to determine the whitening effectiveness and the extent of physical and chemical degradation.

The first part of the thesis, Paper for Publication, describes the significance of the study, the methods and materials used for testing, and a presentation of test results. The article content and format was selected for submission to a publication such as Studies in Conservation, the Journal of the International Institute for Conservation of Historic and Artistic Works, to whom the article will be submitted first. The second part of the thesis, Appendix, presents a more extensive review of literature and list of references as well as a more complete tabulation of research data.

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Department of Clothing, Textiles and Interior Design
College of Home Economics
Manhattan, Kansas 66506

ABSTRACT

Naturally yellowed, historic undyed cotton samples were treated with selected bleaching methods to determine whitening effectiveness and the extent of physical and chemical degradation. Evaluated were samples chemically bleached with hydrogen peroxide solutions at concentrations of .03% and .06% and oxidized for 1/2, 1, and 3 hours, and samples sun bleached in natural sunlight for 4, 16, and 32 hours. Findings showed that the greatest Whiteness Index values were obtained with chemically bleached samples oxidized for 3 hours and the sun bleached samples exposed to sunlight for 32 hours. Physical and chemical degradation assessed by breaking strength, methylene blue, and copper number tests, revealed that significant changes in the physical or chemical properties of the samples had not occurred as a result of the various bleaching treatments.

1. INTRODUCTION

Cellulosic fibers are susceptible to the action of light, air, and atmospheric contaminants, resulting in the continuous discoloration and deterioration of undyed as well as dyed textiles. Body oils, perspiration, dirt, aging, etc. also may result in staining and fabric discoloration. The restoration of a textile's original whiteness often necessitates the use of a bleaching treatment resulting in an improvement of appearance but at the risk of damaging the fabric. The appearance of aged, undyed historic textiles can frequently be improved by mild wet cleaning and bleaching methods. If not properly applied, however, bleaching treatments may be detrimental to historic textiles, especially those already in a fragile or damaged condition.

Limited research is available that documents the use of bleaching treatments on historic white textiles. The uncertainty of the extent of damage produced by such treatments discourages the publication of institutions' bleaching practices. The purpose of this study was to evaluate the suitability of selected bleaching treatments for use on historic, white cotton textiles. The bleaching methods investigated in this study were sun bleaching and chemical bleaching with hydrogen peroxide. After bleaching, the cotton specimens were assessed in terms of efficiency of the bleaching processes and the effects of the methods on the physical and chemical properties of the cotton fibers.

Sun bleaching of cellulosic textiles, one of the oldest bleaching

treatments, was particularly popular in Europe from the mid sixteenth century until the development of chemical bleaches in the nineteenth century. Prior to the introduction of cotton in Europe, sun bleaching had been a method of whitening linen. During the middle of the eighteenth century Holland possessed a monopoly on sun bleaching, receiving linens and sometimes cottons from England [6, 10, 12]. The Dutch method of sun bleaching involved steeping the fabric in solutions of a weak lye and hot potash lye for about a week, after which the fabric was given a thorough washing and then was steeped in buttermilk for a few days. Finally, the fabrics were moistened and spread out on the grass for several months [6]. Similar sun bleaching processes were practiced in the home well into the nineteenth century [1, 2, 4, 14]. The application of sun bleaching for textile conservation was investigated in this study since it does not require the use of chemical oxidizing agents and may provide an alternative form for improving fabric whiteness.

The discovery of the first chemical bleaches, chlorine and chloride of lime, in the late eighteenth century contributed to the development of more superior bleaching agents in the nineteenth century. Increased production of chemical bleaches prompted by the Industrial Revolution resulted in the rapid expansion of the commercial bleaching industry in the United States. In 1818 L. J. Thenard discovered hydrogen peroxide, which is widely used today in the textile industry for bleaching greige goods since it is considered safe for most fibers. It became a commercially important bleaching agent for textiles in the 1920's after it became available in large quantities at economic prices [8].

A review of literature revealed chemical bleaching methods that have been used include solutions of hydrogen peroxide and sodium perborate, a derivative of hydrogen peroxide. Other bleaching studies have

established that the efficiency, as well as the degrading effects of the bleach bath, is dependent on the concentration, pH, additives, and temperature of the bleach bath [13]. Of the chemical bleach bath formulations suggested in literature for historic conservation work, large discrepancies existed in concentration and temperature. Rice [9], for example, suggested solutions of hydrogen peroxide varying in concentrations between 0.1% and 0.5% using bath temperatures ranging from 38 to 49°C (100 to 200°F). At the Smithsonian, McHugh [7] reported bleaching white historic textiles in a $\approx 1\%$ bleach bath containing 30 ml of hydrogen peroxide, 10 g of sodium perborate, and 1000 ml of distilled water at room temperature. A more widely known chemical bleaching formulation in conservation work was developed at the Laboratory for Textile Technology at Delft University of Technology, Netherlands [5]. This method utilized a 1.5% room temperature solution which contained 5 g of sodium metasilicate, 5 volumes of hydrogen peroxide, and 1 liter of distilled water.

2. EXPERIMENTAL

2.1. Fabrics

The test fabric used in this study was obtained from a yellowed, nineteenth century women's nightgown. Due to the abundance of this type of garment in Kansas State University's costume collection and the the extensive mechanical damage in the center front portion of the gown, it was felt that the garment would be suited for research purposes, since conservation seemed impractical and results from naturally yellowed cotton would be more valid than test results from artificially aged cottons. The fabric was a 88 x 78 unmercerized, lightweight, plain weave cotton bastiste with a yarn construction of a single ply, Z twist.

Before bleaching, the gown was wet cleaned. The garment was first presoaked in neutral distilled water for 30 minutes, after which it was immersed in a .25% solution of AATCC detergent 124 for another 30 minutes. During the first and last minutes, the gown was lightly tamped with the finger tips to ensure penetration of the solution and provide gentle agitation to facilitate cleaning. Next, the garment was rinsed 5 times in neutral distilled water, drained, and allowed to dry on glass. After wet cleaning, twenty samples, each measuring 20.32 x 27.94 cm, were cut and randomly assigned to the various bleaching methods. As would be expected, the yellowed condition of the test fabric was not consistent throughout, and several pronounced areas of discoloration existed. For the most part, these areas were avoided in cutting the samples.

2.2 Chemical Bleaching

Since the samples were allowed to dry subsequent to wet cleaning, they were presoaked in neutral distilled water for 20 minutes prior to bleaching to prevent rapid or uneven absorption of the bleaching liquor. Randomly selected samples were immersed in two separate bleach solutions at room temperature, having concentrations of .03% (1 volume) and .06% (2 volume). Table 1 presents the concentrations of the various components used in the bleach bath formulations.

Table 1. Components Used in Bleach Bath Formulations

Components	Quantities	
	.03% H_2O_2 Soln.	.06% H_2O_2 Soln.
Hydrogen peroxide (30% solution), H_2O_2	10 g	20 g
Sodium (meta) silicate, Na_2SiO_3	5 g	5 g
Sodium hydroxide, NaOH	.5 g	.5 g
Sodium carbonate, Na_2CO_3	1.5 g	1.5 g
Distilled water	983 g	973 g
TOTAL	1000 g	1000 g

The general procedures described by McHugh [7] and Leene [5] were followed for chemical bleaching. The samples were placed on fiberglass screens, lowered into the bleach baths, and soaked for 10 minutes. Supported by the fiberglass screen, the samples were lifted out of the bleach bath, held above the bath to drain for 1 minute, and then placed in polyethylene bags to oxidize further. Separate sets of specimens were oxidized in the polyethylene bags for 1/2, 1, and 3 hours. Upon completion of the bleaching, samples were rinsed thoroughly 5 times in neutral distilled water and dried flat on a plate glass surface.

2.3. Sun Bleaching

Samples were exposed to natural sunlight between the hours of 10 A.M. and 2 P.M. in an AATCC Outdoor Exposure Cabinet, without glass cover, for 4, 16, and 32 hours during the months of May and June, 1978. The general procedures in AATCC Test Method 111B - 1975, Weather Resistance: Exposure to Natural Light and Weather, were followed, since a standard test method specifically for sun bleaching was not available. The exposure cabinet, located on the roof of Justin Hall, Kansas State University, Manhattan, Kansas, faced due south and the rack sloped at a 45° angle. An Epply SP-S pyranometer, mounted on the horizontal, recorded the total radiation in Langley units. (Note: Most weather stations measure radiation received on the horizontal, however, in many standard test methods for evaluating weather resistance and lightfastness to natural light, the samples are mounted on a 45° angle. Since total radiation received on the horizontal differs from that received on a slope, the total radiation in Langley units during each exposure period was adjusted to correspond to the amount of radiation received on the horizontal.) The samples exposed for 4 hours received 327 Langleys, for 16 hours received 1,261 Langleys, and for 32 hours received 2,477 Langleys. Replications were exposed on the same days to minimize fluctuations in ultraviolet radiation, humidity, temperature, etc. Only clear, sunny days were selected for testing. Samples were exposed dry since moisture would have added another variable and because research has shown the evaporation of water will accelerate the production of oxycellulose at the cellulose-water-air interface [3]. The average temperature and relative humidity of the test days were 20°C (68°F) and 28%, respectively.

2.4. Color Difference

The degree of whiteness obtained with the various bleaching methods was evaluated according to the procedure in AATCC Test Method 110-1975, Reflectance, Blue, and Whiteness of Bleached Fabrics, using the following Whiteness Index:

$$WI_{(ASTM\ E\ 313)} = 4Z\% - 3Y = 4B - 3G$$

Instrumental measurement of whiteness values were calculated using a Hunterlab D25-M tristimulus colorimeter and Tektronix 31 programmable calculator. The average values for five specimens were computed for each of the two replications.

2.5. Physical Tests

Breaking strength values of the test samples after sun bleaching and hydrogen peroxide bleaching were determined according to ANSI/ASTM D 1682-64 (Reapproved 1975), Breaking Load and Elongation of Textile Fabrics, using the One Inch Raveled Strip Method. The average of five test specimens was taken for each of the two replications. The Scott Model J Tester was used with a 3-inch nominal gauge length.

2.6. Chemical Tests

The extent of cellulosic oxidative degradation was quantitatively assessed with the methylene blue and copper number tests. The colorimetric method outlined by Skinkle [11] was used to determine the absorption of methylene blue by the carboxylic acid groups formed by alkaline oxidation. Samples weighing 1.25 g were shaken in a conical flask for 18 hours in 25 ml of M/2500 methylene blue solution. After shaking, the remaining solution was collected and the absorbance readings were compared with a standard M/2500 methylene blue solution in a Bausch

and Lomb Spectronic 20 colorimeter.

The Schwalbe-Braidy copper number test [11] was used to evaluate the number of aldehyde or reducing groups present in oxycellulose. One hundred milliliters of a boiling alkaline copper sulfate solution, containing copper sulfate, sodium bicarbonate, and sodium carbonate, were poured over each 2.5 g sample of the test fabric in a conical flask. The flasks containing the samples were then placed in boiling water for 3 hours, after which the contents of the flask were filtered and washed. The filtrate was discarded, and the samples were treated with an acidic ferric alum solution, washed with dilute sulfuric acid, and titrated with a standard N/25 potassium permanganate solution. The amount of copper present in the solution was calculated by the given formula:

$$\text{Copper number} = \left[100 \times \frac{(\text{volume of } \text{KMnO}_4 \text{ used}) - (\text{volume of } \text{KMnO}_4 \text{ for blank})}{.044 \times \frac{\text{milliequivalent (weight of copper)}}{\text{dry weight of sample}}} \right]$$

2.7. Statistical Analysis

The statistical procedure used to assess the effects of bleaching method, concentration, oxidation time, and exposure time on the degree of whiteness obtained and breaking strength was the analysis of variance test. The least significant difference test was used to determine where significant differences occurred. A 5% significance level was used in the statistical analysis.

3. RESULTS

3.1. Effects of Bleaching on Whiteness

This study evaluated the degree of whiteness and the extent of degradation obtained in historic white cotton, chemically bleached with hydrogen peroxide solutions at concentrations of .03% and .06% for 1/2, 1, and 3 hours, and sun bleached for 4, 16, and 32 hours. The Whiteness Index (WI) values for the test specimens are presented in Figure 1. In the statistical analysis, time was the only significant effect ($p=.007$). In general, a progressive increase in whiteness resulted as exposure time increased in sun bleaching and as oxidation time increased with hydrogen peroxide bleaching.

In the analysis, the Whiteness Index values of all of the chemically bleached samples were significantly different from the unbleached controls. Of the Whiteness Index values for the fabrics bleached in the .03% H_2O_2 solution, the samples oxidized for 3 hours became the whitest (i.e. exhibited the highest WI values). The whiteness levels obtained for these samples were significantly greater than for those samples oxidized for 1 hour. The difference between 1 hour and 1/2 hour oxidation periods, however, was not significant.

Fabrics bleached with the .06% H_2O_2 solution became progressively whiter as oxidation time increased. Again, the samples oxidized for 3 hours (.06% - 3 hours) reached the highest level of whiteness. Only a slight increase in the mean values occurred between 1 and 3 hours of

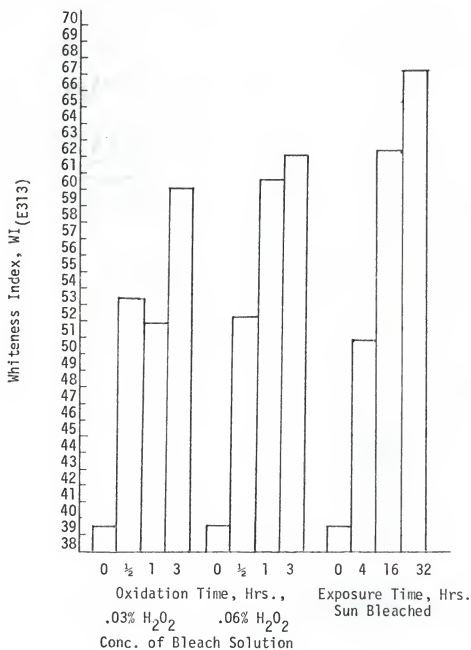


Fig. 1 Whiteness Index Values for Chemically Bleached and Sun Bleached Samples.

oxidation. A significant difference in WI values was obtained for the samples bleached in the .06% H_2O_2 solution and oxidized 1/2 and 1 hour.

Concentration of the bleach bath was not a significant effect and significant differences in whiteness were not observed for the samples bleached in the .03% and .06% H_2O_2 solutions at the various oxidation periods, except after the 1 hour oxidation period. Statistically, no significant difference occurred in the mean whiteness values obtained for the samples bleached with the .03% H_2O_2 solution and oxidized for 3 hours (.03% H_2O_2 - 3 hours) and the samples bleached with the .06% H_2O_2 solution and oxidized for 1 hour and 3 hours (.06% H_2O_2 - 1 hour, .06% H_2O_2 - 3 hours).

The sun bleached samples progressively increased in whiteness after 4, 16, and 32 hours of exposure. Samples receiving 32 hours of sun light exposure exhibited the greatest increase in whiteness among the chemically bleached and sun bleached fabrics. The greatest color change occurred during the first 4 hours of light exposure, with a mean ΔWI value of 13 units. Whiteness of all sun bleached samples were significantly different from the control. Results showed a significant difference in the degree of whiteness obtained in the samples sun bleached for 4 hours and 16 hours; however, no significant difference was obtained between samples sun bleached for 16 hours and 32 hours.

When comparing the sun bleached and chemically bleached samples, no significant differences were found among the samples that had the least amount of change in whiteness. These were the samples bleached in the .03% H_2O_2 solution and oxidized for 1/2 hour and 1 hour, the samples bleached in the .06% H_2O_2 solution and oxidized for 1/2 hour and the samples sun bleached for 4 hours. The samples obtaining the greatest degree of whiteness were the samples sun bleached 32 hours and 16 hours,

respectively. In addition, no significant difference in the WI values existed among these samples which had the greatest degree of whiteness.

In summary, the whitening efficiency of the selected treatments were dependent on the time allotted for oxidation in chemical bleaching and the exposure periods in sun bleaching. Samples receiving 32 hours of sun light obtained the greatest color change. The concentration of the bleach solutions proved not to be a significant variable. Samples treated in .03% and .06% H_2O_2 solutions applied for 3 hours reached approximately the same level of whiteness.

3.2. Effect of Bleaching on Breaking Strength

Breaking strength was used for assessing the extent of fiber degradation attributable to chemical bleaching and sun bleaching. The samples bleached in the .03% and .06% hydrogen peroxide solution were evaluated after 1/2, 1, and 3 hours of oxidation, and the sun bleached samples were evaluated after 4, 16, and 32 hours of outdoor light exposure. Presented in Table 2 are the results of the breaking strength tests.

The analysis of variance statistical test applied to the breaking strength means showed no significant differences in breaking strength among all levels of chemical bleaching and sun bleaching. None of the bleaching treatments investigated caused a significant loss in breaking strength when compared to the control.

3.3. Chemical Tests

Methylene blue and copper number tests were utilized for assessing the extent of chemical degradation which occurred in the chemically bleached and sun bleached samples after each oxidation and exposure period. As evidenced by the data for these tests (see Table 2), no

Table 2 Comparison of Breaking Strength, Methylene Blue, and Copper Number Means for Sun Bleached and Hydrogen Peroxide Bleached Fabrics.

	Exposure Time (In Hours)	Breaking Strength (In Pounds)	Methylene Blue (Millimoles/100 gm dry sample)	Copper Number (grams/100 gm dry sample)
Control		11.64	86	1.53
Sun Bleaching	4 (337 Lang)	13.02	87	1.49
	16 (1261 Lang)	13.49	87	1.76
	32 (2447 Lang)	12.72	87	2.05
H ₂ O ₂ Bleaching (% Conc. - Oxidation Time)	.03- $\frac{1}{2}$	12.48	86	1.61
	.03-1	10.71	86	1.73
	.03-3	12.66	85	1.20
	.06- $\frac{1}{2}$	12.03	86	1.61
	.06-1	12.69	86	1.50
	.06-3	11.09	86	1.56

significant change occurred in the chemical structure of the cellulosic samples subsequent to bleaching.

The methylene blue test showed no appreciable differences in the carboxyl group content of the test samples before and after each bleaching treatment. Carboxyl groups are indicative of excessive oxidation under alkaline conditions. Similarly, the copper number tests indicate the absence of aldehyde or reducing groups on the cellulosic fibers which are produced when cellulose is excessively bleached or oxidized under acidic conditions, resulting in a breakdown of the glycosidic linkages. The values obtained were very similar and ranged between 1.20 and 2.05 grams per 100 gram dry sample. The results of these two chemical tests indicated that the extent of chemical degradation from the various bleach treatments was minimal.

3.4 Scanning Electron Microscope

After completion of the various bleaching treatments, fibers from the test samples were examined by a scanning electron microscope. No observed morphological changes had occurred in the treated cellulosic fibers. Scanning electron micrographs of non-wet cleaned, wet cleaned, and bleached fibers showed random degradation throughout the fiber structure (see Figures 2 through 7). Typically, some individual fibers showed severe degradation while neighboring fibers were comparatively unaffected (see Figures 4 through 7). Degradation was characterized by numerous rough surface irregularities, grooves, ridges and diagonal cracks or splits along the fibril patterns, with cracks often penetrating into the secondary layers (see Figure 3). Small, partially detached, fragments or particles were common along the fiber surface (Figure 5). The SEM photographs were representative of the general observations made



Fig. 2 Cotton Fiber from Historic Test Fabric Before Wet Cleaning (2000X).



Fig. 3 Cotton Fiber from Historic Test Fabric After Wet Cleaning (2000X).



Fig. 4 Cotton Fiber from Historic Test Fabric After Wet Cleaning (800X).



Fig. 5 Cotton Fibers Bleached in .03% Hydrogen Peroxide Solution and Oxidized for 3 Hours (800X).



Fig. 6 Cotton Fibers Bleached in .06% Hydrogen Peroxide Solution and Oxidized for 3 Hours (800X).



Fig. 7 Cotton Fibers Sun Bleached for 32 Hours (2477 Langleys) (800X).

on the cotton test samples before and after bleaching.

4. CONCLUSIONS

The appearance of undyed, historic cotton fabrics often may be improved by treating the textile with mild bleaching solutions. In addition, sun bleaching out-of-doors also has potential as a viable alternative bleaching method. Investigated in this study were the bleaching efficiency and degradative effects of hydrogen peroxide bleaching and sun bleaching on historic, undyed cotton fabrics. Test samples were soaked in .03% and .06% hydrogen peroxide solutions and oxidized for 1/2, 1, and 3 hours, and sun bleached for 4, 16, and 32 clock hours.

Findings showed that the whiteness levels obtained with chemical bleaching were dependent on the time allotted for oxidation. The greatest increase in whiteness occurred in hydrogen peroxide bleached samples that were oxidized for 3 hours. The changes in whiteness resulting from sun bleaching also increased as exposure time increased. Whiteness Index values showed that the greatest change in whiteness was obtained for the samples exposed to sun light for 32 hours. These samples' values were not significantly different, however, from the values obtained for the samples exposed to the sun for 16 hours and for the samples chemically bleached in the .06% hydrogen peroxide solution and oxidized for 3 hours.

Results showed insignificant differences in the Whiteness Index values obtained with samples bleached in a .03% hydrogen peroxide solution and oxidized for 3 hours ($.03\% \text{ H}_2\text{O}_2$ - 3 hours) and samples bleached in a .06% hydrogen peroxide solution and oxidized for 1 and 3 hours

(.06% H_2O_2 - 1 hour, .06% H_2O_2 - 3 hours). Thus, a shorter oxidation time with approximately the same amount of whiteness resulting was possible with the .06% solution oxidized for 1 hour. On the basis of this research one could select a lower concentration (.03%) for a longer oxidation time (3 hours), or a higher concentration (.06%) for a shorter oxidation period (1 hour). The tightness of the weave and yarn construction could influence which treatment would be preferred.

Breaking strength, methylene blue, and copper number tests were used to assess the effects of the bleaching methods, concentrations, and oxidation and exposure times on the physical and chemical properties of cotton cellulose, thereby determining the extent of oxidative degradation. Breaking strength test results found no significant differences in strength among the unbleached, chemically bleached and sun bleached samples. In addition, there were no significant differences among the copper number and methylene blue test values for the untreated controls and the chemically and sun bleached samples. Both sun bleaching and chemical bleaching with .03% hydrogen peroxide solution are suitable methods applicable to conservation work for improving the appearance of historic, white cotton textiles, without causing fiber degradation.

Upon completion of the various bleaching treatments all samples exhibited an increase in whiteness. Samples which obtained the highest levels of whiteness became sufficiently white for display purposes and remained historically accurate. If greater whiteness levels are desired than were obtained in this study, stronger bleach solutions or longer oxidizing periods may be feasible if the bleaching conditions are evaluated prior to use to determine if the solution(s) are mild enough to avoid fiber degradation.

While sun bleaching resulted in the greatest amount of whitening,

possible limitations should be noted for its use in textile conservation. Total radiation reaching the earth is dependent upon a variety of factors including time of year, time of day, climatic conditions, atmospheric contaminants, and etc. The amount of radiation absorbed by a samples is, therefore, more relevant than actual hours of exposure. In this study sun bleaching was conducted in an area with low levels of pollution. The types and amoung of pollution in a geographical area may be a significant factor in the extent of photodegradation during outdoor exposure. In areas with high levels of atmospheric contaminants, very short periods of outdoor exposure may result in rapid textile degradation. The effect of moisture on sun bleached fabrics in relation to the degree of whiteness and degradation is yet another variable which requires further study, particularly if large amounts of contaminants exist in the atmosphere.

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APPENDIX

The Appendix contains a more extensive review of literature and list of references as well as a more complete tabulation of research data not found in the Paper for Publication.

REVIEW OF LITERATURE

Introduction

Historic costumes and textiles are important artifacts for understanding past societies and civilizations, since they often reflect societal norms, values, technological developments, and political and economic structures, and also may serve as primary sources for historic research. Today many museums, universities, and historical societies maintain collections of textile works of unprecedented craftsmanship that are undergoing continuous deterioration due to insufficient knowledge concerning proper conservation techniques. The historical significance of costumes, textiles, and related items has resulted in an increased interest in preserving and maintaining these articles for present and future generations. Consequently, the area of costume and textile conservation has been receiving considerable attention. Textiles conservation is an interdisciplinary field which encompasses many disciplines. Ideally, a conservator should have some background in anthropology, sociology, chemistry, physics, and art history as well as costume, history, and textile science.

Textile conservation is a relatively new science and, as a result, many chemical and physical techniques, suitable for conservation work, remain unexplored. Minimal research, for example, is available on the bleaching methods applicable for cleaning and restoring the whiteness

and appearance of historic textiles. Many collections contain an abundance of white historic cotton garments and laces which could benefit aesthetically if safe bleaching techniques were developed. Yet many museums in the United States avoid bleaching because of the uncertainty of the effects, while others indiscriminately approach the problem.

A limited amount of literature is available which evaluates the suitability of different bleaching methods for improving the appearance of historic textiles. Various concentrations of hydrogen peroxide solutions, for example, have been used at several museums but with limited controls. One source briefly mentioned the possibility of sun bleaching [75]. In order for a bleaching method to be suitable for textile use, especially in the conservation area, it must whiten the fabrics without causing extensive physical or chemical degradation.

The purpose of this study was to compare the effectiveness of selected bleaching methods for historical white cotton fabric and to determine the amount of physical and chemical degradation which occurred. The two major bleaching methods evaluated were chemical bleaching with hydrogen peroxide at two different concentrations and sun bleaching.

History of Cotton

The origin of cotton remains uncertain. Botanical research maintains that primitive cotton plants were not a suitable fiber source for textile purposes. The earliest identified cotton used in textiles was found in a fragment of cloth from Mohenjo-Daro in the Indus Valley of Pakistan, dated 1760 B.C. \pm 115 [85]. Archaeological and literary evidence suggests that the cultivation of fiber-bearing cotton plants began in India from where it may have spread to Egypt. The Egyptians also were masters of spinning and weaving and supposedly invented a pre-shrinking

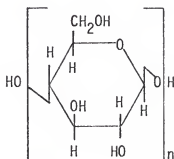
process [72].

Little is known about the diffusion of the cotton plant to other parts of Asia, the Middle East, Africa, and Europe. Cotton was brought to the Greeks in 300 B.C. by the armies of Alexander the Great [68]. Eastward expansion to China, where it was considered a decorative plant, is speculated not to have occurred until the seventh century or much later [68]. According to a Japanese legend, cotton was introduced in that country around 800 A.D. when a Hindu ship wrecked off the coast of Japan [55,68]. By the tenth century cotton industries developed around eastern centers of cultivation, many producing specialty cloths or garments for export.

Cotton was first produced in southern Europe around 100 A.D., where it remained until transported to northern Europe by Crusaders. Cotton was generally known throughout the world by 1500 A.D., but cotton fabrics were often confused with those of linen and wool [67,83]. During the seventeenth century, European commerce felt the impact of the expanding textile industry. In 1599 the British East India Company began importing printed and painted cottons in Europe, which increased the popularity of cotton. The demand for these cottons became so great that by the early eighteenth century wool and linen producers in England and silk producers in France could not compete successfully. As a result, sumptuary laws forbidding the wearing and production of cotton goods were enacted in these countries [45,77]. By mid century these bands had been lifted, resulting in the extensive manufacture of printed cotton cloth. Production of printed cotton fabrics aided the economic growth of England and America. From this point on, the history of cotton consists mainly of developments in machinery for production, bleaching, dyeing, and printing of cotton textiles.

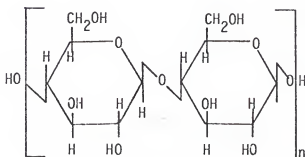
Cellulosic Chemistry

Raw cotton is composed of approximately 94% cellulose and 6% impurities, consisting of waxes, pectins, proteins, pigments, and inorganic compounds [45]. After preliminary scouring and bleaching processes, the cotton fiber contains approximately 99% cellulose. Cellulose is a high polymeric, long chain compound chemically described as poly (1,4-B-D anhydroglucopyranose). The basic unit of cotton cellulose is a six carbon membered pyranose ring which is called the anhydroglucose unit. Each polymer chain contains approximately 10,000 glucose units.



Anhydroglucose Unit

The repeat unit in cellulose is the B-1,4 anhydro cellobiose unit, constructed from the condensation of B-glucose molecules linked through the 1 and 4 carbons.



Anhydro Cellobiose Unit

The long chains of cellulose molecules are arranged into two types of regions, crystalline and amorphous, the latter of which comprises between 5 to 15% of the fiber [45]. In the crystalline regions the chains are closely packed together and lie parallel to each other; whereas, in the amorphous region the chains of molecules are randomly arranged. The molecules in the crystalline regions are stabilized by intramolecular hydrogen bonding between the hydroxyl groups [55].

The chemical reactivity of cellulose is chiefly attributed to the hydroxyl groups along the polymer chains. Each anhydroglucose unit contains one primary hydroxyl group located in the sixth carbon position and two secondary hydroxyl groups in the second and third carbon positions. In general, primary alcohols are more reactive than secondary and tertiary alcohols.

Cotton is very durable and is capable of withstanding high temperatures; although, at temperatures exceeding 170°C (338°F) the fiber will yellow and degrade. Alkalies and cold dilute acids do not readily degrade cotton, but it does have low resistance to hot dilute acids or cold concentrated mineral acids. Acids can attack the glucosidic linkage, resulting in a shorter chain length and a decrease in strength. [45]

Causes of Degradation and Discoloration of Textiles

Discoloration and deterioration of historic white cotton textiles results from a variety of factors, many of which stem from oxidation processes. Oxidation is a general term which is often used to describe the ageing process. Chemically oxidation may be defined as either the combination of oxygen with other elements and compounds, or, more generally, the loss of electrons. In the latter case, elements other than oxygen may be involved [54]. The oxidation of alkalies that have remained on

partially oxidized fibers may result in the formation of brown stains on textiles. Another type of brown stain is attributed to the continuous evaporation of water at the cellulose-water-air interface in which oxycellulose is formed [2].

Discoloration and fiber degradation may be catalyzed by atmospheric oxygen in the presence of light and moisture. The cotton substrate may be degraded either directly or by substrate additives which oxidize, thereby, producing reactive species that subsequently degrade the cellulosic fiber. In general, pure cellulose is not readily degraded by light; however, dyes, impurities and/or finishing agents present on the fabric may accelerate fabric degradation and deterioration. The tendency for starch to turn yellow serves as an example of this process. [3,24,84] In addition, certain areas in a historic printed textile may be severely degraded while undyed areas remain unaffected. As a result, holes develop in certain areas within the textile, depending on the design.

Yellow spotting on textiles is commonly attributed to the absorption of body oils, perspiration, and urine by the fabric. Extreme heat or scorching, such as that caused by a hot iron, is yet another source of yellowing and cellulosic degradation. Further sources of dark colored stains include foodstuffs, blood, rust, greases, smoke and soot stains, paints, and ink. Unwanted colored substances also may result from dyes bleeding, either from other areas within the textile or from another colored textile [75].

Other sources of cellulosic deterioration stem from microbial attack of two general types. Rot occurs when enzymes secreted by a micro-organism attack and degrade the fibrils in the secondary wall structure of the cotton fiber, resulting in fiber strength losses.

The feeding action of micro-organisms on the outer surface of cellulose, without degrading the underlying cellulose, is known as mildew. The organisms responsible for mildewing or rotting are fungi, bacteria, and actinomycetes (a family of micro-organisms that resembles both bacteria and fungi) [15].

Fungus and bacteria reproduce in the presence of free oxygen; therefore, their growth is accelerated on cotton textiles when the proper combination of humidity and temperature are present. Fungi favor unpurified cotton cellulose in which more suitable conditions for growth are present [11,15]. Cellulose that is acidic in nature and/or is treated with finishes such as starch, dextrin, and tallow are especially susceptible to fungi deterioration. Because bleached fabrics do not contain as many impurities and generally have a higher pH level than unbleached fabric, they are more resistant to microbial attack. Bacteria growth is most rapid at pH levels between 7 and 8 [11]. Microbial attack is characterized by a musty odor and the formation of various stains that are attributed to either the color of the organism itself or to enzymatic degradation products. The stains may vary from white to yellow, pink, green, brown, or red [11,15,38].

Cellulosics are vulnerable to insect attack, although not as often as protein fibers. Insect damage to cellulosics may be caused by termites, silverfish, cockroaches, and fire brats [38,56,87]. Termite attack can be detected by remaining dirt particles on fabrics from tunnels built to preserve a supply of moisture [38]. Silverfish and cockroaches attack sizing present on cellulosics. Insect excretments compound the damage done to textiles, in addition to causing severe fabric soiling [56].

Chemical attack from atmospheric contaminants is another source of

deterioration and discoloration. The action of sulphur dioxide, for example, is one of the most destructive chemicals on all fibers. Sulphur dioxide (SO_2) combines with water to form sulfurous acid (H_2SO_3), which can further oxidize to sulfuric acid (H_2SO_4), a very strong acid [11,25,53].

In addition to atmospheric chemicals, deposition of air born dirt containing iron, sulphur dioxide, and other metal catalysts, may be harmful to fabrics, dyes, and finishes. Other damaging constituents of air born dirt includes sand, dust, lint, and other earthy matter. The rough edges of the dirt particals work their way between fibers, yarns, and crevices, thus causing abrasion damage to the fabric as well as increasing the possibilities of microbial and insect attack [87].

Chemical Bleaching and Sun Bleaching

The word bleach comes from the Anglo-Saxon word "blācon" which means to become pale [61]. Often times bleaches are misused as detergents to remove unwanted dirt on fabrics; but bleaches are not surfactants and, as such, will not remove dirt. The three primary functions of bleaches are 1) to remove certain stains, 2) to improve or retain fabric whiteness, and 3) to kill micro-organisms [55].

History

The bleaching of textiles is an art that was first understood and practiced by the ancient Chinese and Hindus, according to Walton [83]. It was through these peoples that the Phoenicians obtained their knowledge of bleaching. They, in turn, passed the art onto the Egyptians from whom the Greeks and Romans gained the knowledge. Little is known about these early bleaching methods. The Romans are thought to have whitened wool and linen by using the fumes of burning sulfur [43,78]. They

stretched their fabrics over semi-oval wicker frames, and then burned sulfur beneath the frame. As a final step, the fabrics were brushed with fuller's earth [43].

In 1742 a Jesuit missionary priest, Father Coeurdoux, recorded an early bleaching process practiced in India, that consisted of first beating cotton fabrics with a stone, immersing them in water in which sheep droppings had been soaked, and then washing the fabrics in clear water. Subsequent to washing, the cotton textiles were spread out in the sun for three days while being periodically sprinkled with water [61].

Beginning in the sixteenth and continuing through the seventeenth and eighteenth centuries, the process of sun bleaching cotton and linen textiles became an important part of the economic structure of western Europe. Sun bleaching had been a method of whitening linens which had been practiced prior to the introduction of cottons in Europe [76,83]. One of the earliest mentions of sun bleaching was recorded by Shakespeare in England, during the sixteenth century. He spoke of the "whitsters" employed to do the bleaching. The lengthy processes commenced with a pre-treatment step which consisted of steeping the fabrics in cow excrement, sour milk, and then in lye. For the next week, boiling hot potash was poured over the fabrics. The linens were then thoroughly washed and put into wooden vats of buttermilk and held under pressure for five or six days, after which they were spread out on the grass fields, kept wet, and exposed to sunlight for several months. If satisfactory results were not obtained, the entire process would be repeated. The process of steeping in lyes was known as "bucking", whereas bleaching was called "crofting" [61,64,83].

Demand for whitened goods increased during the eighteenth century. In the early part of this century, sun bleaching became a national

industry in Ireland. By the middle of the eighteenth century, Holland possessed a monopoly on the bleaching trade in Europe. Linens, and sometimes cottons from England, were shipped to Holland in March and returned in October [64,76,83]. The Dutch method of sun bleaching consisted of first steeping the linens in a weak lye solution and then in a hot potash lye, for about a week. After this the fabric was given a thorough washing and steeped in buttermilk for several days. Finally, the fabrics were moistened and spread out on the grass for several months. The impurities in the linens were rendered soluble by the acid constituents in the buttermilk [64].

The first step in the development of chemical bleaching occurred in 1756, when Dr. Home of Edinburgh realized that actions of acids in buttermilk could be obtained faster and more economically through the substitution of sulphuric acid. The next major step in chemical bleaching was the discovery of chlorine in 1774 by a chemist named Scheele. Eleven years later, another chemist, named Berthollet, discovered chlorine's bleaching action on cellulose. Tennant and McIntosh discovered the process for making dry chlorine of lime or bleaching powder by saturating quicklime with chlorine and, hence, revolutionized the bleaching industry. When first discovered, bleaching powder was very toxic, inconvenient, and had an obnoxious odor [35,43,76,77,83,84]. By 1830, a stable form was available, making bleaching powder practical for commercial use on cellulosic textiles. It soon became the principle agent for cotton and linens, but has been virtually replaced today by sodium hypochlorite [80]. In 1818 L. J. Thenard discovered hydrogen peroxide which is currently used in the textile industry for bleaching greige goods, since it is considered safe for most fibers. It became a commercially important bleaching agent for textiles in the 1920's after

it became available in large quantities at economic prices [66,84].

Increased availability of chemical bleaches in the nineteenth century, marked a major step toward the expansion of the bleaching industry during the Industrial Revolution. The development of machinery capable of processing large quantities of fabrics enabled the bleaching industry to keep up with the increasing linen and cotton production [68,76].

While industry continued to research chemical bleaching treatments, the bleaching method which prevailed in the home was sun bleaching. Earle [47], in Home Life in Colonial Days, wrote about the forty different processes of wetting, washing, and grass bleaching which were conducted on linens before they became pure white. The term "grassing" was often used to describe the sun bleaching process.

Home bleaching methods, published in late nineteenth century literature, recorded processes which included scalding the goods in suds, immersing them in hot lye solution, rinsing and allowing them to lie in the sun for several weeks. Frequent dampening of goods increased the degree of whiteness obtained [39,41,44,50,52,86]. Bleaching during the winter was accomplished by laying the fabrics on the snow [44]. Sun bleaching was often the preferred method of bleaching because of the belief that chemical bleaching weakened cellulosic fabrics more than sun bleaching [39,40,50,86].

Physics of Light

Light is a form of radiation, traveling in waves. The distance between two peaks of the wave is called the wavelength and is usually measured in fractions of a meter. Wavelengths can be expressed in microns, μ (10^{-4} cm), in millimicrons, $m\mu$ (10^{-7} cm) or nanometers, or in

Angstrom units, A (10^{-8} cm). The energy potential of the wavelengths are related to their position in the electromagnetic spectrum; the shorter the wavelength, the greater the energy.

The portion of the electromagnetic spectrum with the greatest energy potential and shortest wavelengths are the gamma rays and X-rays. Next on the continuum is the ultraviolet region, consisting of wavelengths between 4 and 400 nm. About 10% of the sun's energy is in this region. Wavelengths shorter than, and including the ultraviolet rays, are also known as actinic rays. Following the ultraviolet region of the spectrum is the visible portion, defined by the International Commission on Illumination (C.I.E.) as the wavelengths between 380 and 780 nm [59]. One half of the sun's energy is concentrated in this region. The remaining portions of the electromagnetic spectrum with the longer wavelengths are the infrared, microwave and radiowaves, respectively.

The ultraviolet region of the electromagnetic spectrum is of particular interest due to its photochemical effects on cellulose. It can be divided into three regions; the Schuman region (120-185 nm), the far ultraviolet region (200-300 nm), and the near ultraviolet region (300-400 nm) [59] (See Fig. 8).

Intensity of terrestrial sunlight is determined by a variety of factors, including season of the year, time of day, altitude, elevation above sea level, atmospheric turbidity, and the thickness of ozone [16,27]. Studies by Luckiesh and by Colbentz [59] illustrate seasonal ultraviolet intensity peaks; for example, 62% of the yearly total radiation is supplied during the months of May, June, July, and August in comparison to 7% of ultraviolet radiation supplied during the months of November, December, January, and February. As the height of the sun increases, so does the ultraviolet intensity, producing the greatest

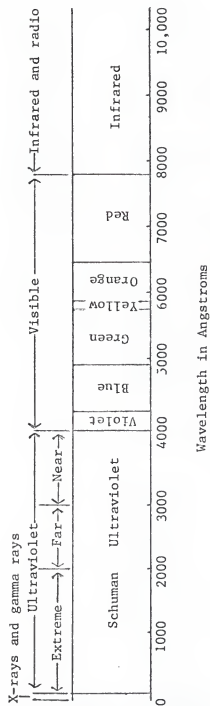


Fig. 8 Electromagnetic Spectrum (Adapted from Koller⁵⁹).

intensity in the middle of the day.

Window glass also affects the spectral distribution of the light reaching an object. Ordinary window glass, in thicknesses of two millimeters or more, absorbs ultraviolet waves, shorter than 300 nm [9,63,87]. Robinson and Reeves [27] stated that clear glass absorbs light up to at least 320 nm and usually much higher.

Total radiation emitted from the sun can be measured and expressed in units called Langleys (cal/cm^2) or in kilojoules per square meter (kJ/m^2). Both units are used to measure the intensity of solar radiation at various wavelengths, eliminating discrepancies due to time of year, climatic conditions, etc.

Classes of Chemical Bleaches

Bleaches are categorized into two broad classes; reducing and oxidizing bleaches. A reducing bleach functions by removing oxygen from a substance, whereas an oxidizing agent adds oxygen or similar electro-negative atoms to a substance. Both oxidizing and reducing bleaching agents have been used to whiten textiles and help to remove impurities (i.e. stains, dyes, etc.); however, the loss of color in a substance is not necessarily an indication that the impurities have been removed. Reducing bleaches are not widely used in the bleaching of textiles because the whiteness produced by the bleaching action is not always permanent due to the constant supply of oxygen in the air which causes a counteraction [48]. Reducing compounds include sodium hydrosulfite, sodium sulfide, zinc hydrosulfite, and zinc formaldehyde sulfoxylate.

The oxidizing bleaches are divided into four principal types: chlorine and non-chlorine bleaches, each with a liquid and dry form. Chlorine bleaches are used in bleaching of cotton, linens, and other

cellulosics, but they are not suitable for protein fibers because they degrade and discolor wool and silk. In addition, chlorine bleaches are not used in historic textile conservation because of their rapid and harsh bleaching action [22,24]. Liquid chlorine bleaches consist of the hypochlorite (OCl^-) bleaches such as calcium hypochlorite, sodium hypochlorite, and sodium chlorite. Dry chlorine bleaches perform similarly to liquid chlorine bleaches but are less versatile for non-laundry purposes. Chloride of lime is an example of a dry chlorine bleach.

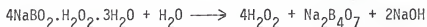
Non-chlorine liquid oxygen bleaches frequently utilize hydrogen peroxide as the active oxidizing agent. Their oxidizing potential has been limited because, until recently, they were unable to have builders combined with them. Subsequently, the dry form of oxygen bleaches which contain additives, such as sodium carbonate and other builders, have greater bleaching potential. When combined with water, the active bleaching agent formed is hydrogen peroxide [82]. Sodium perborate and potassium permanganate are examples of dry non-chlorine oxygen bleaches.

Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) is a weak acid. A commercial 100 volume hydrogen peroxide has a pH level between 2.5 and 4.5 [48]. In an acid solution it remains stable, but at pH levels above 7 it will begin to disassociate. Ionization occurs most rapidly at pH levels above 11.5 [84] and is accelerated by heat, light, and metals. To maintain its strength, hydrogen peroxide should be stored in a cool, dark place. Hydrogen peroxide is a safe bleach for proteins, cellulosics, and most colored fabrics [24,73,84]. Its gentle bleaching action results in less fabric deterioration, strength loss and/or chemical modification than chlorine bleaches [24,73,75]. At one time, it was believed the nature

of the chemical reaction of hydrogen peroxide was due to the oxidation action of nascent oxygen, which had decomposed from the hydrogen peroxide; however, this theory is no longer supported. Scheller [84] believed the perhydroxyl ion to be the active species. Other researchers reviewed by Taher and Cates [30] include Wood and Richmond, and Steinmiller and Cates, who suggested the bleaching mechanism was attributed to free radicals formed by hydrogen peroxide and other peroxy compounds, rather than oxygen.

A derivative of hydrogen peroxide is sodium perborate, a white crystalline powder. Although its exact chemical structure is not certain, it is empirically written as $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$. When dissolved in water, sodium perborate breaks down into an alkaline solution of borax and hydrogen peroxide.



Sodium perborate's mild bleaching action is attributed to its slow rate of ionization and constant pH level. Because hydrogen peroxide's rate of oxidation is faster than sodium perborate's, it is more appropriate for shorter bleaching periods [42].

Bleach Bath Formulations

A properly balanced bleach bath is necessary for controlled bleaching. When working with aged textiles, a diluted, mild bleach bath is essential. Studies by Oesterlerting and co-workers [84] have found that concentration, pH, temperature, and type of alkali used in a bleaching formula, are all important factors in controlling the bleaching potential of a bath.

Concentration

The strength of a hydrogen peroxide solution is indicated by either the volume of available oxygen, liberated from one unit of volume of the hydrogen peroxide liquor, or by the percentage of the liquor in the solution [81]. The relationship between volume strength and percentage is shown in Table III.

Table 3. Comparison of Hydrogen Peroxide in Volume Strength and Percentage by Weight

VOLUME STRENGTH	PERCENTAGE H_2O_2 BY WEIGHT
1	0.3
2	0.6
3	0.9
5	1.5
10	3.0
100	27.5
131	35.0
197	50.0

[49]

Alkalies

Safe and effective bleaching conditions for celluloses require alkaline aqueous solutions. Ward [84] stated the best pH for peroxide bleaching is between 10.7 and 10.9. The proper pH level is achieved through the addition of alkalies to the bleach bath.

Alkalies can be of two types, weak or strong depending on the ionization potential of the compound. Examples of strong alkalies used in bleaching solutions are potassium hydroxide, also known as caustic

potash (KOH), and sodium hydroxide or caustic soda (NaOH). Sodium and potassium hydroxides exhibit high ionization potentials, whereas, weak alkalis, such as ammonium hydroxide, ionize less rapidly.

Additives

Once the correct pH level is obtained in the bleach bath, it is maintained by the use of additives, called builders. Commonly used builders are sodium carbonate, sodium (metal) silicate, borax, and various phosphates. Sodium carbonate is one of the oldest builders used in bleaches. Its use is limited since it may cause the shrinkage of woolen fabrics and bleeding of dyes [24]. Sodium silicate is used very successfully as a builder in bleach baths. According to Moore [81], it is the only alkali that ensures good peroxide stability. The probable reason is that it forms complexes with the metallic ions which have a powerful catalytic effects. It has been recommended that the alkali content of the peroxide liquor be adjusted so that 60 to 80% of the total alkalinity is supplied by silicate ($2.5 \text{ SiO}_2 : 1\text{Na}_2\text{O}$) and the other 20 to 40% is supplied by caustic soda (NaOH) [84].

Temperature

The higher the temperature of the bleach bath, the faster the rate of bleaching action. When hydrogen peroxide is heated, it disassociates more readily. The rate of chemical reaction doubles for every 10°C (18°F) increase in temperature, thus, even the mildest bleach may damage fabrics when high temperatures are used [48]. Elevated temperatures also increase the danger of damage to fragile or weakened cellulosic textiles. In commercial hydrogen peroxide bleaching baths, the recommended temperatures are between $90\text{--}100^\circ\text{C}$ ($194\text{--}200^\circ\text{F}$) [81].

Bleach Solutions for Historic Textiles

Formulations

Chemical bleaching with sodium perborate and hydrogen peroxide and sun bleaching are methods that have been employed in textile conservation to improve the whiteness and appearance of fabrics. Of the chemical bleach bath formulations suggested in the literature, large differences in concentration and temperature existed. For example, Plenderleith and Werner [73] recommended a room temperature bleach solution containing hydrogen peroxide (6% w/w) and sodium silicate. Aqueous solutions of hydrogen peroxide and sodium perborate have been used by Rice [24]. For the hydrogen peroxide solutions, he suggested bleach bath concentrations between .01 and .05% to be used at temperatures ranging from 38-49°C (100-200°F). At the Smithsonian, McHugh [14] reported bleaching white historic textiles in a room temperature bleach solution containing hydrogen peroxide (2% w/w) and sodium perborate (.7% w/w). A widely used chemical bleaching formulation in conservation work was developed at the Laboratory for Textile Technology at Delft University of Technology, Netherlands. This method utilized a room temperature solution which contained 5 g of sodium hydroxide, 5 g of sodium carbonate, 20 g of sodium metasilicate, 5 volumes (1.5%) of hydrogen peroxide, and 1 liter of water. Rice [24] and Leene [60] suggested a pH of 10 for bleaching purposes.

Historic textiles may be bleached so that they are aesthetically pleasing. Varying philosophies exist, however, on the ethics of such treatments. One viewpoint maintains that only techniques which would prevent further deterioration of a textile should be employed and restorative procedures such as bleaching would destroy historical

accuracy. Opposing philosophies are concerned with aesthetic results and believe in depicting a relic as it would have been seen during its era. Often times this would involve replacing parts of the original item or the utilization of various cleaning methods.

Whether or not a historic cotton textile can be successfully bleached depends on the condition of the textile. Textiles that have been severely degraded may not be able to withstand wet cleaning or mild bleaching treatments. A thorough diagnosis of the textile and a possible determination of the origin of discoloration should be conducted prior to bleaching.

Procedures

The techniques used in wet cleaning and chemical bleaching of historic textiles are very similar in that the fabrics must be supported at all times during the wet cleaning process, since aged fibers are especially weak and susceptible to damage when wet. By laying the textile on a fiberglass screen, extra support is provided to the textile, in addition to facilitating ease of handling. The screen is then used to lower and raise the textile to and from the cleaning or bleaching solutions. Ironing of historic textiles is undesirable, therefore, flat textiles should be placed on glass to dry in order to prevent wrinkling [14,65,60].

Wet cleaning and bleaching are best conducted in shallow vessels, large enough so that the textile or garment can lie flat. Plastic trays, such as those used by photographers, are suitable for smaller pieces. For large items, sinks can be constructed by using large wooden frames lined with plastic. Sinks or utensils made of metals or stainless steel are not recommended for bleaching since metals cause a more rapid

ionization of the oxidizing agent and may result in degradation of delicate or damaged textiles [42,75].

Before a textile is bleached, it is usually wet cleaned. If an item is allowed to dry before bleaching, presoaking in distilled water is desirable to prevent rapid or uneven absorption of the bleach solution. Before the prewetted items are immersed in the solution, the bleach bath should be thoroughly mixed and the pH monitored. Enough solution should be used to substantially cover the textile. Large quantities of liquid places unnecessary weight on the item and may be harmful. Occasional light tamping with the finger tips supplies moderate agitation.

Based on the assumption that short immersion periods are safest for textiles, McHugh [65] and Leene [60] allowed pieces to remain in bleach solution approximately 5 minutes. Subsequent to immersing the textiles in the bleach solution, they were lifted from the bath, the excess solution was removed, and then they were placed in polyethylene bags to oxidize further. According to these researchers, the time allotted for oxidation is dependent upon the results desired, but usually ranged between 1 and 3 hours. The process was completed by thoroughly rinsing the textiles, making certain the final rinse was neutral, and allowing the items to dry.

Rice [24], and Plenderlieth and Werner [73] used different time allotments for bleaching. Rice, for example, allowed items to remain in a hydrogen peroxide bleaching solution between 10 to 20 minutes, after which, the pieces were rinsed and dried. If satisfactory results were not obtained, the process was repeated. Plenderlieth and Werner, on the other hand, soaked pieces from 12 to 16 hours.

Cellulosic Degradation

Photodegradation

Photochemistry mainly is concerned with the physical and chemical reactions which take place when molecules are exposed to radiation in the ultraviolet and visible regions of the electromagnetic spectrum. Electromagnetic radiation is composed of waves of mass less units, called photons or quanta, which travel through space [5,7,16]. The absorption of light by a molecule is dependent upon the chemical structure of the molecule and energy of the waves being emitted [5].

If the radiation is absorbed by an object, an increase in vibrational and rotational energy will result, and electrons will be excited to higher energy levels [5,7,16,27]. When light is absorbed, the energy of the molecule increases by an amount equal to the energy of the photon which is:

$$E = h\nu = hc/\lambda$$

where "h" is Planck's proportionality constant (6.2×10^{-27} erg sec), "c" is velocity, and "v" and " λ " are the frequency and wavelength of light [16].

The excited molecule may then lose the absorbed energy a) by heat, b) by the emission of radiant energy in the form of fluorescence, c) by undergoing a chemical change within the molecule, d) by collision and transfer of the energy to another atom or molecule [5].

Photochemical processes are governed by two laws: 1) the Grotthus-Draper law which states that only radiations which are absorbed by a substance may cause a chemical reaction, and 2) the Stark-Einstein law (or law of photochemical equivalence) which states that one atom or molecule is activated for every photon that is absorbed [5,7].

The wavelengths found to be most destructive to cellulose are believed to be below 350 nm. A review of literature by Appleby [1] reported studies, one by Brown and another by Oguri and Takei, which found the most deteriorating rays for cellulose below 360 and 364 nm, respectively.

Photochemical processes are very complex and are usually regarded as being oxidative in nature. There are two general types of reactions which may occur and cause degradation to cellulosic fibers. These are photolysis and photosensitization.

Photolysis

Photolysis is described as the true photochemical reaction of cellulose. It readily occurs in pure cellulose at wavelengths in the far ultraviolet region of the spectrum, but may take place in the near ultraviolet (300-380 nm) and visible range (380-780 nm) at much reduced rates because of the smaller amounts of energy produced in these regions [8]. Because most ultraviolet rays do not reach the earth, photolysis does not take place except under controlled, artificial light sources [27]. The breakdown, which occurs under this exposure, is thought to be caused by the photolysis of cellulose chains, leading to the cleavage of the carbon-to-carbon or carbon-to-oxygen linkages [11,16].

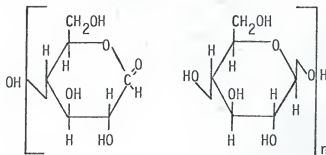
Photosensitization

Photosensitization is the secondary and most important process of photochemistry. The degradation which occurs in the process is the action between light and the presence of a second substance, such as oxygen, moisture, certain dyes and pigments, and certain metallic salts or metals which act as sensitizers [8,11,16,27]. The sensitizer absorbs the light energy and transfers it to the substrate. Damage by photosensitization is extensive because the majority of cellulosic textiles

are not in a pure form, but contain many impurities, dyes, and finishes. Chemically excited sensitizers can attack cellulose, breaking the molecular chains into shorter units, and thereby weakening the glycosidic linkages so that they are more readily attacked and ruptured by oxygen. In certain instances, the reaction rate is increased by the presence of moisture [3,11,16]. Products formed by this reaction, are a reducing type of oxycellulose [11].

Hydrocellulose

Hydrocellulose is the product formed by the reaction of acids on cellulose, resulting in chain scission at the glycosidic linkages, and the formation of aldehyde or reducing groups ($-CHO$) [11,55,79]. The production of hydrocellulose is accompanied by a loss in tensile strength and lower heat resistance. Fehling's solution and the copper number test are examples of chemical tests that are used to quantify the extent of oxidative degradation attributed to acid hydrolysis.



Hydrocellulose

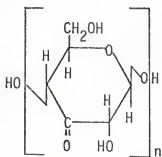
Oxycellulose

Cellulose is readily attacked by a variety of oxidizing agents. Extensive oxidation of cellulose can result in the formation of several degradation products, given the general name of oxycellulose.

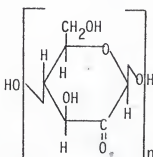
The oxycellulose products formed, are dependent upon the pH of the bleaching solution and the type of oxidizing agent [55]. Chemical attack can occur at either the primary or the two secondary alcohol groups; however, the former are more reactive. Oxidative degradation products can be divided into two types, either reducing or acidic.

In acid bleach bath, for example, aldehyde (CHO) or reducing groups are formed in cellulose. Kenyon [55] and Singh [28] discussed oxycellulose of the reducing type. The presence of aldehyde or reducing groups result in high copper number (i.e. the amount of cuprous oxide formed per 100 gram samples of cotton), but low methylene blue absorption. There are three possible points of attack on the cellulose molecule:

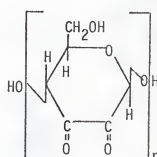
- 1) Attack at one or both of the secondary alcohols (carbons 2 and 3), changing them to ketones without breaking the pyranose ring.



Ketone

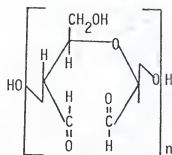


Ketone



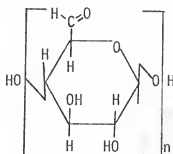
Di-Ketone

- 2) Attack at the secondary alcohols, forming aldehydes and rupture of the pyranose ring.



Di-Aldehyde

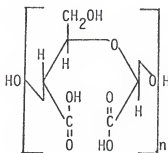
- 3) Attack at the primary alcohol, (carbon 6) changing it to an aldehyde.



Aldehyde

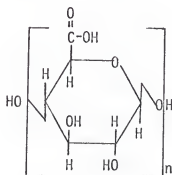
Alkaline oxidizing bleach baths result in the formation of carboxylic acid groups (COOH), rather than aldehyde groups, which are identified by increased methylene blue absorption and low copper number. Here again, there are several points of attack:

- 1) Further attack of the aldehyde groups at carbons 2 and 3 to carboxyl groups (COOH).



Di-Carboxyl

- 2) Oxidation attack at the carbon 6 alcohol group to a carboxyl group.



Carboxyl

Generally, oxidation and hydrolysis of cellulose is heterogeneous; that is, the chemical attack usually is random throughout the fiber. Chemical attack is more rapid in the amorphous regions than in the crystalline regions of the fiber [45]. Some acids, however, have specific points of attack. Oxycellulose is very weak and becomes weaker when wet; therefore, historic textiles that have been subject to numerous bleachings during their life time, should be handled carefully.

Evaluation of Test Methods

Whiteness

The efficiency of a bleaching process is frequently measured in terms of whiteness, such as in AATCC Test Method 110-1975 [37]. In many instances whiteness is associated with purity, as well as cleanliness. According to Hunter [57], a white surface is one that reflects strongly throughout the visible portion of the electromagnetic spectrum. As the per cent reflectance relative to a given standard (i.e. MgO) increases and becomes more uniform, the surface usually appears whiter to the eye.

Textiles which deviate from white usually absorb more or reflect less light in the blue region rather than in the yellow or upper portion of the visible spectrum. As a result, the material appears yellowish. Whiteness can be improved by several methods. In the case of chemical or sun bleaching, blue absorbing impurities are oxidized, reduced or removed which increases reflectance at shorter wavelengths (380-500), thereby making the reflectance more uniform in the visible region. Fluorescent whitening agents function by converting ultraviolet light to blue light, which makes the fabric appear bluer. Blueing agents are blue dyes which, when applied to the fabric, reduce the reflectance in other parts of the spectrum, relative to the blue end.

A variety of scales have been developed for measuring whiteness using tristimulus values. Hunter [57] reviews the mathematical equations for computing numerous whiteness scales. The formula for one of the most frequently used whiteness scales and the one used in this study is:

$$WI_{(ASTM\ E\ 313)} = 4Z\% - 3Y$$

In this equation, as in many whiteness scales, the blue component is given more weight since it is more important than the lightness component. Reflectometers and tristimulus colorimeters are used for measuring whiteness.

Breaking Strength

Strength is a general term which refers to the ability of a material to resist strain or rupture induced by external forces (ANSI/ASTM D123-77). Breaking strength usually is determined by measuring the force required to break or rupture a fabric, when held under tension, and is expressed in either kilograms of force (kgf) or as pounds of force (lbf) [58,62].

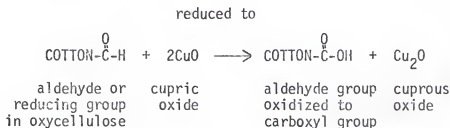
Several types of tensile testers have been developed: the constant-rate-of-extension (CRE), the constant-rate-of-load (CRL), and the constant-rate-of-traverse (CRT). Specimens may be tested by the Grab Test Method, the Ravelled Strip Test, or the Cut Strip Test. Standard testing conditions (relative humidity $65\% \pm 2$; temperature $20^{\circ}\text{C} \pm 2^{\circ}$) should be maintained during testing as they may have a significant influence on test results.

Copper Number and Methylene Blue Tests

The copper number and methylene blue absorption are quantitative tests that are frequently used for evaluating cellulosic oxidative

degradation products. As discussed previously, oxycellulose is a general term for a series of degradation products, produced by the action of oxidizing agents on cellulose [46,55,81]. Oxycellulose degradation products, which contain aldehyde or reducing groups, are evidence of oxidation in an acid medium; whereas, carboxyl groups are produced when oxidative degradation occurs in an alkaline medium.

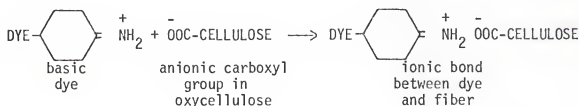
The copper number test is used to quantify the number of aldehyde groups present in oxycellulose and is defined as the number of grams of copper reduced from cupric oxide (CuO) to cuprous oxide (Cu_2O) in an alkaline solution by 100 grams of dry sample.



According to Skinkle [79] the original copper number test was carried out with Fehling's solution but has since been modified because of the high alkalinity of the solution which, in the presence of air, caused a progressive oxidation of the cellulose substrate. The Schwalbe-Braidy [79] method, which utilizes a modified solution of alkaline copper solution, is widely used. After boiling the samples for 3 hours in the copper solution, they are filtered, washed, and then treated with an acidic feric alum solution. The ferric alum wash is then titrated with a standard N/25 potassium permanganate solution.

The methylene blue test evaluates the number of carboxyl groups (COOH) present in oxycellulose that have been formed by alkaline oxidation. Oxycellulose of the alkaline type possess a great affinity

for basic dyes such as methylene blue. If the oxycellulose formed contains carboxyl groups, it should behave as a weak organic acid. In testing, the basic dyes are in solutions as salts of weak acids [55]. When oxycellulose is treated in solutions of known strength and buffered to a known pH (usually 7), the hydroxyl groups react by absorbing amounts of dye equal to the carboxyl content.



The concentration of the methylene blue absorbed by the fabric is determined by titrating the solution with naphthol yellow S or by the colorimetric method and is expressed in millimoles per 100 grams of dry sample. Tendering due to alkaline oxidation may not become very apparent in the methylene blue test until fibers are treated with alkali [46].

Scanning Electron Microscope.

The scanning electron microscope (SEM) is a highly sophisticated instrument, similar in principle to an ordinary light microscope. First invented in the mid 1930's, the SEM has developed into a widely used research tool for the examination and analysis of microstructural characteristics of solid objects, including composition, surface topography, and crystallography.

One of the most valuable features of SEM, is the large depth of field which allows it to focus on more than one plane, thereby producing 3-dimensional appearances. Another reason for its usefulness stems from the large magnification range possible, which varies from about 5 times

to 100,000 times [4,69,70].

The scanning electron microscope operates on a time sequency technique to produce a micrograph similar to that used in a closed-circuit television system. The system is capable of scanning an entire specimen or zooming in on one particular area. The elctron source in the SEM is a heated tungsten cathode. As the electrons are emitted, they are demagnified and focused by a series of lenses. When the controlled beam reaches the specimen, secondary electrons are released. These electrons are then collected by a detector and amplified in a scintillator, onto a fluorescent screen display system. Samples that do not conduct electricity, such as cotton, must be treated with a thin layer of conductive metal, which is evaporated onto it to hold the surface of the sample at a constant electric potential [70].

Several studies illustrate the applicability of scanning electron microscopy in textile research. Specific studies on cotton deterioration, under various conditions, have been conducted. Research by Hock [10], Porter and Goynes [19], and Trip, Moore, and Rollins [32] dealt with changes in surface topography of chemically treated cotton. Other studies by Porter, Carra, Tripp, and Rollins [18] were concerned with degradation of cotton, attributed to various micro-organisms.

STATISTICAL TEST RESULTS

Table 4 Hourly Radiation Recorded for April, 1978 by Kansas State University Weather Station at Outdoor Exposure Site.

[illegible]

Table 6 R-Value for Converting Incident Radiation on a Horizontal Surface, H_i , to Incident Radiation on a Surface Having a Slope of 45 Degrees, H_r . Valid for Manhattan, Kansas (Latitude 39.1 Degrees North).

HOUR DATE	10	11	12	13	14	HOUR DATE	10	11	12	13	14
APRIL 1	1.20	1.20	1.21	1.20	1.20	MAY 1	1.00	1.03	1.03	1.03	1.00
APRIL 2	1.19	1.20	1.20	1.20	1.19	MAY 2	1.00	1.02	1.03	1.02	1.00
APRIL 3	1.18	1.19	1.19	1.19	1.18	MAY 3	0.99	1.02	1.03	1.02	0.99
APRIL 4	1.17	1.18	1.19	1.18	1.17	MAY 4	0.99	1.01	1.02	1.01	0.99
APRIL 5	1.16	1.18	1.18	1.18	1.16	MAY 5	0.98	1.01	1.02	1.01	0.98
APRIL 6	1.16	1.17	1.17	1.17	1.16	MAY 6	0.98	1.01	1.01	1.01	0.98
APRIL 7	1.15	1.16	1.17	1.16	1.15	MAY 7	0.98	1.00	1.01	1.00	0.98
APRIL 8	1.14	1.16	1.16	1.16	1.14	MAY 8	0.97	1.00	1.01	1.00	0.97
APRIL 9	1.14	1.15	1.15	1.15	1.14	MAY 9	0.97	0.99	1.00	0.99	0.97
APRIL 10	1.13	1.14	1.15	1.14	1.13	MAY 10	0.96	0.99	1.00	0.99	0.96
APRIL 11	1.12	1.14	1.14	1.14	1.12	MAY 11	0.96	0.99	0.99	0.99	0.96
APRIL 12	1.11	1.13	1.13	1.13	1.11	MAY 12	0.96	0.98	0.99	0.98	0.96
APRIL 13	1.11	1.12	1.13	1.12	1.11	MAY 13	0.95	0.98	0.99	0.98	0.95
APRIL 14	1.10	1.12	1.12	1.12	1.10	MAY 14	0.95	0.98	0.98	0.98	0.95
APRIL 15	1.09	1.11	1.12	1.11	1.09	MAY 15	0.94	0.97	0.98	0.97	0.94
APRIL 16	1.09	1.11	1.11	1.11	1.09	MAY 16	0.94	0.97	0.98	0.97	0.94
APRIL 17	1.08	1.10	1.11	1.10	1.08	MAY 17	0.94	0.97	0.97	0.97	0.94
APRIL 18	1.08	1.09	1.10	1.09	1.08	MAY 18	0.93	0.96	0.97	0.96	0.93
APRIL 19	1.07	1.09	1.09	1.09	1.07	MAY 19	0.93	0.96	0.97	0.96	0.93
APRIL 20	1.06	1.08	1.09	1.08	1.06	MAY 20	0.93	0.96	0.96	0.96	0.93
APRIL 21	1.06	1.08	1.08	1.08	1.06	MAY 21	0.92	0.95	0.96	0.95	0.92
APRIL 22	1.05	1.07	1.08	1.07	1.05	MAY 22	0.92	0.95	0.96	0.95	0.92
APRIL 23	1.05	1.07	1.07	1.07	1.05	MAY 23	0.92	0.95	0.96	0.95	0.92
APRIL 24	1.04	1.06	1.07	1.06	1.04	MAY 24	0.92	0.95	0.95	0.95	0.92
APRIL 25	1.03	1.06	1.06	1.06	1.03	MAY 25	0.91	0.94	0.95	0.94	0.91
APRIL 26	1.03	1.05	1.06	1.05	1.03	MAY 26	0.91	0.94	0.95	0.94	0.91
APRIL 27	1.02	1.05	1.05	1.05	1.02	MAY 27	0.91	0.94	0.95	0.94	0.91
APRIL 28	1.02	1.04	1.05	1.04	1.02	MAY 28	0.91	0.94	0.94	0.94	0.91
APRIL 29	1.01	1.04	1.04	1.04	1.01	MAY 29	0.90	0.93	0.94	0.93	0.90
APRIL 30	1.01	1.03	1.04	1.03	1.01	MAY 30	0.90	0.93	0.94	0.93	0.90
						MAY 31	0.90	0.93	0.94	0.93	0.90

Table 7 Hourly and Total Radiation Received by Sun Bleached Samples Mounted on a Vertical Slope of 45°, Converted from Readings on Horizontal Surface.

Date (1978)	Langleys 11 A.M.	(Hours Ending at Central Standard Time)		Total Langleys
		12 P.M.	1 P.M.	
April 21	77.11	85.54	85.75	326.84
April 23	78.11	86.88	90.09	339.71
April 24	77.59	78.32	56.15	290.77
May 2	62.8	76.5	83.43	303.92
May 8	62.27	73.8	73.53	278.2
May 9	62.47	75.64	83.6	300.51
May 13	62.51	76.05	83.95	307.38
May 14	60.42	74.28	81.34	299.34

Table 8 Hourly Temperature Recorded for April, 1978 by Kansas State University Weather Station, Manhattan, Kansas.

UNITED STATES DEPARTMENT OF COMMERCE WEATHER BUREAU																											
STATION		Manhattan												Data												Date	
STATION		April, 1978												Temperature												Date	
STATION		DATA SHEET, HOURLY RECORDS												Temperature												Date	
Hour	Day	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	Hour	Day
1	64	60	55	54	54	52	50	50	53	56	58	62	64	66	67	68	68	66	66	64	63	63	63	63	63	1	4
2	66	65	62	60	59	64	64	58	70	70	72	73	76	76	78	78	79	76	74	70	67	65	62	59	57	2	4
3	64	59	59	63	64	61	58	50	53	59	62	64	66	68	69	70	70	69	66	60	57	54	54	54	54	3	4
4	55	56	56	56	54	55	55	56	55	56	57	58	59	60	61	62	63	64	65	66	64	62	59	56	56	4	4
5	56	55	54	52	51	52	55	60	64	67	71	73	74	74	74	74	72	69	64	62	58	58	57	57	57	5	4
6	69	69	69	69	67	66	65	66	69	72	74	78	80	84	84	82	80	78	74	72	71	70	70	70	70	6	4
7	67	67	66	66	65	64	64	66	69	72	72	74	77	78	74	74	70	69	66	62	50	49	48	47	47	7	4
8	46	46	46	45	45	45	46	48	50	52	54	54	55	54	54	54	48	42	49	46	42	41	41	40	40	8	4
9	38	38	38	37	37	37	38	44	52	56	60	62	64	65	66	67	66	64	62	58	58	57	57	58	58	9	4
10	56	56	58	56	54	52	54	56	59	62	60	64	67	69	69	68	66	60	56	50	48	46	44	44	44	10	4
11	52	41	40	38	39	37	40	51	54	57	60	63	64	65	66	67	65	54	51	50	49	48	47	46	46	11	4
12	37	37	37	37	37	37	38	43	46	48	49	51	51	51	50	50	49	48	48	48	48	47	46	46	46	12	4
13	47	47	47	48	48	48	48	48	49	51	51	50	50	49	48	46	46	46	46	46	46	46	46	46	46	13	4
14	46	46	46	46	46	46	47	47	48	48	49	50	51	52	54	54	54	50	49	47	46	46	46	46	46	14	4
15	47	48	48	48	48	48	49	50	51	52	54	54	54	54	54	54	50	49	47	46	46	46	46	46	46	15	4
16	42	42	42	42	43	43	44	44	46	46	46	48	48	48	48	48	47	44	42	42	41	41	42	42	42	16	4
17	36	36	36	36	36	36	38	41	44	48	51	52	54	52	52	51	50	48	44	40	38	37	36	36	36	17	4
18	35	32	30	30	32	36	44	48	52	54	58	59	60	59	58	57	56	55	54	52	50	49	49	49	49	18	4
19	48	48	49	49	49	49	50	50	51	56	60	64	68	68	68	67	67	60	53	50	47	44	44	44	44	19	4
20	41	40	40	41	39	41	44	54	59	64	67	71	72	73	74	74	74	70	66	60	58	58	58	58	58	20	4
21	61	61	60	64	62	62	62	62	64	64	64	64	64	64	64	64	64	64	64	64	64	64	64	64	64	21	4
22	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	22	4
23	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	23	4
24	40	36	37	40	45	50	56	62	65	67	68	69	70	70	70	70	68	66	62	59	57	53	51	51	51	24	4
25	52	52	50	51	52	54	58	61	66	69	71	68	68	69	71	70	68	66	62	60	58	57	56	56	56	25	4
26	56	55	54	52	54	54	56	59	61	62	66	70	71	70	71	70	70	68	66	65	64	63	62	62	62	26	4
27	62	60	60	68	57	56	59	59	62	64	66	70	72	74	76	76	75	74	70	62	60	50	59	58	58	27	4
28	57	56	58	60	58	56	55	55	56	56	57	57	57	58	58	59	59	58	58	57	56	55	55	55	55	28	4
29																										29	4
30																										30	4

Continued Weather Bureau, Washington, D. C. 20540

Table 9 Hourly Temperatures Recorded for May, 1978 by Kansas State University Weather Station, Manhattan, Kansas.

WS Form 250-110
(2-77)

UNITED STATES DEPARTMENT OF COMMERCE, WEATHER BUREAU
DATA BRANCH, COUNTY RECORDS

STATION													DATE												
Manhattan													May, 1978												
A. M.													Data												
Temperature													P. M.												
1	2	3	4	5	6	7	8	9	10	11	12	13	1	2	3	4	5	6	7	8	9	10	11	12	13
1	55	54	53	51	50	50	50	50	50	50	51	52	55	54	56	57	57	56	56	52	50	48	46	44	
2	43	44	44	42	41	41	42	48	52	56	57	59	60	61	60	60	60	59	58	56	54	52	50	49	48
3	47	48	47	46	47	46	48	48	48	46	50	51	50	54	54	54	54	52	51	51	50	50	49	48	
4	47	48	47	46	46	46	47	48	50	51	51	54	54	54	54	52	52	50	49	48	46	45	45	42	
5	40	38	40	42	42	43	45	45	54	53	56	57	60	60	60	60	60	60	58	56	55	55	54		
6	53	52	51	50	48	46	45	45	44	44	44	44	44	44	45	46	46	45	42	40	39	38	35	34	
7	48	49	49	50	50	50	51	51	53	54	56	54	52	54	57	60	60	60	58	55	52	51	50	50	
8	50	50	49	48	47	46	50	54	60	61	63	64	66	67	68	68	66	60	58	57	54	52	51		
9	51	49	48	49	49	49	52	55	62	64	66	68	70	71	72	72	72	68	64	59	59	55	53		
10	57	54	51	52	50	51	56	64	69	74	78	76	79	80	78	76	76	74	72	70	69	68	68		
11	71	67	65	66	64	62	66	68	72	72	74	76	77	76	74	76	78	76	71	66	64	62	61		
12	60	60	60	61	62	60	60	58	56	61	66	60	64	64	67	66	64	62	60	58	56	55			
13	52	50	48	46	45	45	50	52	58	62	68	70	71	72	72	72	72	70	65	61	56	54	52		
14	55	53	52	50	48	46	45	56	62	68	70	71	72	72	72	72	72	70	65	61	56	54	52		
15	54	52	51	50	48	46	45	56	62	68	70	71	72	72	72	72	72	70	65	61	56	54	52		
16	58	56	56	54	53	52	54	58	63	66	68	70	73	73	72	71	69	66	64	64	63	61			
17	61	61	61	62	62	62	62	63	67	68	70	73	74	76	77	76	75	74	70	67	65	64	63	62	
18	63	67	66	65	64	64	64	67	70	72	74	78	83	85	86	87	86	84	82	80	78	76	70	67	
19	66	66	66	64	62	60	61	60	62	64	67	68	70	71	71	72	72	72	69	66	63	62	60		
20	58	56	55	54	53	52	55	59	64	66	68	70	71	72	73	74	72	71	68	66	64	62	63	62	
21	62	61	60	59	59	60																			
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31																									
Notes																									Notes

Comments: Weather Bureau, Washington, D. C. 20

Table 10 Hourly Humidity Recorded for April, 1978 by Kansas State University
Weather Station, Manhattan, Kansas.

STATION		Manhattan		Manhattan		DATA		Humidity		P. M.		Miles		Size		Date	
Date	April, 1978	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
2	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
3	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
4	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
5	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
6	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
7	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
8	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
9	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
10	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
11	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
12	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
13	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
14	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
15	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
16	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
17	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
18	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
19	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
20	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
21	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
22	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
23	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
24	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
25	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
26	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
27	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
28	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
29	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
30	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76
31	38	42	60	70	75	76	76	76	76	76	76	76	76	76	76	76	76

Continued on Weather Bureau, Washington, D. C. 20540

Table 11 Hourly Humidity Recorded for May, 1978 by Kansas State University
Weather Station, Manhattan, Kansas.

WS Form 50b-11D
1-6-78

UNITED STATES DEPARTMENT OF COMMERCE WEATHER BUREAU
DATA ENTRY - HOURLY RECORDS

Station		Manhattan												Humidity												Row	
Date		A. M.												P. M.												Max	
		May, 1978																									
		1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12		
1	70	70	70	72	66	60	52	47	42	40	37	34	34	34	30	32	28	28	28	30	32	38	40	44	47	1	
2	52	55	53	60	58	56	46	38	29	26	24	22	22	22	22	22	22	22	23	26	30	34	36	43	49	2	
3	50	51	53	59	54	56	75	54	50	52	48	43	36	32	32	32	32	32	32	34	36	40	42	47	53	3	
4	58	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	4	
5	45	47	49	60	72	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	5	
6	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	6	
7	100	98	95	92	83	87	84	52	44	36	35	33	28	27	25	24	24	28	35	38	45	54	54	54	7		
8	52	57	65	68	66	64	54	44	35	30	28	25	24	20	21	20	19	21	27	36	45	54	54	54	8		
9	55	65	70	78	82	90	60	48	35	31	27	25	24	23	24	26	30	33	38	43	48	54	54	54	9		
10	56	80	76	84	97	100	88	80	70	62	58	57	55	56	58	76	58	56	56	72	86	96	100	100	10		
11	100	100	100	100	100	98	97	94	98	98	100	100	100	100	100	100	100	100	100	100	100	100	100	100	11		
12	55	58	60	61	66	58	44	42	38	36	33	32	31	31	27	24	22	22	28	34	48	60	63	63	12		
13	75	73	63	96	98	93	74	62	49	35	28	24	23	21	18	18	16	18	20	23	40	47	56	57	13		
14	56	56	52	58	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	14		
15	66	81	86	93	97	100	100	90	70	53	44	42	38	34	33	33	34	35	36	40	46	50	50	54	15		
16	68	68	60	68	68	68	70	70	66	71	64	58	52	50	50	53	60	64	69	79	92	94	93	92	16		
17	93	94	98	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	17		
18	71	81	88	68	66	75	76	74	70	62	54	50	44	44	42	40	38	39	44	49	59	65	70	76	18		
19	80	90	98	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	19		
20	70	70	82	84	88	89	91	92																	20		
21																									21		
22																									22		
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29																									29		
30																									30		
31																									31		

Source: Kansas State University Weather Station, Manhattan, Kansas.

Table 12 Analysis of Variance Test Results for Whiteness Index Means.

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Squares	F	Probability
Treatment	9	1167.181	129.687	15.740	0.0001*
Concentration (C)	1	31.460	31.460	3.818	0.0792
Chemical Bleaching Time (T)	2	137.307	68.653	8.333	0.0074*
C X T	2	51.684	25.842	3.136	0.0876
Sun Exposure Time (S)	2	284.366	142.183	17.257	0.0006*
C X S	1	51.004	51.004	6.190	0.0321*
C X S X Control	1	611.360	611.360	74.203	0.0000*

* .05 level of significance

Table 13 Least Significant Difference (L.S.D.) Test Results for Whiteness Index Means¹.

Sun Bleached for 32 Hours	67.405	*	
Sun Bleached for 16 Hours	62.500	*	*
.06% H ₂ O ₂ Oxidized for 3 Hours	62.060	*	*
.06% H ₂ O ₂ Oxidized for 1 Hour	60.725		*
.03% H ₂ O ₂ Oxidized for 3 Hours	60.055		*
.03% H ₂ O ₂ Oxidized for ½ Hour	53.360		*
.06% H ₂ O ₂ Oxidized for ½ Hour	52.245		*
.03% H ₂ O ₂ Oxidized for 1 Hour	51.900		*
Sun Bleached for 4 Hours	50.980		*
Control	39.485		

¹ Non-significant groupings at 0.05 protection level are connected by columns of asterisks.

Table 14 Analysis of Variance Test Results for Breaking Strength Means.

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Squares	F	Probability
Treatment	9	13.838	1.538	1.108	0.4343
Concentration (C)	1	0.000	0.000	0.000	0.9867
Chemical Bleaching Time (T)	2	0.649	0.324	0.234	0.7957
C X T	2	6.607	3.304	2.381	0.1427
Sun Exposure Time (S)	2	0.603	0.301	0.217	0.8085
C X S	1	5.145	5.145	3.708	0.0830
C X S X Control	1	0.834	0.834	0.601	0.4562

* .05 level of significance

RECOMMENDATIONS FOR FURTHER RESEARCH

This study evaluated the degree of whiteness and the extent of degradation obtained in historic, white cotton fabrics, chemically bleached with hydrogen peroxide solutions at concentrations of .03% and .06% for 1/2, 1, and 3 hours, and sun bleached for 4, 16, and 32 hours. Some suggestions for further research include:

- a) Investigation of the effects of higher hydrogen peroxide bleach bath concentrations on whiteness and extent of degradation.
- b) Evaluation of the degree of whiteness obtained with longer oxidation periods during chemical bleaching and the effects on fiber properties.
- c) A comparison of results obtained with samples allowed to oxidize in hydrogen peroxide bleach bath solution with those oxidized in polyethylene bags.
- d) Evaluation of the effects of the various types and amounts of atmospheric contaminants on cotton fabrics during sun bleaching.
- e) Evaluation of the relationship between sun bleached samples moistened with water and samples exposed dry.
- f) Experimentation with longer exposure times to the sun.

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AN EVALUATION OF SELECTED BLEACHING TREATMENTS
SUITABLE FOR HISTORIC WHITE COTTONS

by

ZOE KATHERINE ANNIS

B.S., Southwest Missouri State University, 1975

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the
requirements for the degree

MASTER OF SCIENCE

Department of Clothing, Textiles, and Interior Design

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1978

The discoloration of undyed, historic cotton textiles is attributed to a variety of factors such as body oils, perspiration, dirt, atmospheric contaminants, and aging. The restoration of a textiles' whiteness often necessitates the application of a mild bleaching solution; however, limited research is available that documents the use of bleaches on white historic textiles. The purpose of this study was to evaluate the efficiency and degradative effects of selected bleaching methods that have potential applicability in the area of textile conservation for improving the appearance of yellowed, undyed cottons.

Separate test samples were chemically bleached with .03% and .06% hydrogen peroxide solutions and oxidized for 1/2, 1 and 3 hours, and sun bleached in natural sunlight for 4, 16, and 32 hours. All samples were wet cleaned prior to bleaching. The chemically bleached samples were presoaked in neutral, distilled water, immersed in the bleach solutions for 10 minutes, and then oxidized in polyethylene bags. Sun bleached samples were mounted on an AATCC Outdoor Exposure Cabinet, without a glass cover, and exposed to natural light between the hours of 10 A.M. and 2 P.M. Total radiation received by the samples was monitored with an Epply SP-S pyranometer.

The efficiency of the various bleaching treatments was evaluated instrumentally by calculating the change on the Whiteness Index (WI) values, using a Hunterlab D25-M tristimulus colorimeter and Tektronix 31 programmable calculator. Physical and chemical degradation was assessed

by breaking strength, methylene blue, and copper number tests. In addition, fibers from the treated samples were visually evaluated for the type and extent of surface damage by means of a scanning electron microscope. An analysis of variance was applied to the data to evaluate the effects of the bleaching treatments on whiteness and breaking strength.

All of the bleaching treatments significantly increased the whiteness of the undyed cotton test fabric, but the degree of whiteness obtained was dependent on the time allotted for oxidation in chemical bleaching and the exposure periods in sun bleaching. The concentrations of the bleach solutions was not a significant variable since the samples treated in .03% and .06% solutions and oxidized for 3 hours reached approximately the same degree of whiteness. Samples receiving 32 hours exhibited the greatest improvement in appearance.

Results also showed no significant differences in breaking strength among all levels of chemical bleaching and sun bleaching; thus, none of the bleaching methods in this study had detrimental effects on fabric strength. This fact was confirmed by the findings from the chemical tests which indicated that the extent of chemical degradation was minimal, as there were no significant changes in the chemical structure of the cotton fabrics subsequent to bleaching.

The scanning electron photomicrographs of the cotton samples before and after wet cleaning and bleaching at each exposure and oxidation level showed no substantial changes had occurred in the morphological characteristics of the treated fibers. Degradation throughout the untreated and treated fibers was random, characterized by surface irregularities, ridges, diagonal cracks, and partially detached fragments along the fiber surface.